AD NUMBER

AD860404

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 15 OCT 1969. Other requests shall be referred to Air Force Materials Laboratory, Wright-Patterson AFB, OH 45433.

AUTHORITY

AFSC ltr dtd 2 Mar 1972

DMIC review

Refractory Metals (Cb, Ta, Mo, W)

OCT 1969

D. J. Maykuth, E. S. Bartlett, and V. D. Barth • October 15, 1969

NUCLEAR POWER GENERATION

Evaluations of selected refractory metals and their alloys are being continued in several nuclear-power-generation studies. The basic reasons for the interest in these materials lie with their inherently good resistance to corrosion by liquid metals and their high strength at elevated temperatures. Current emphasis in these programs encompasses the following:

(1) Determining the compatibility of various new alloys in the liquid metals favored as heat-transfer media, e.g., potassium, sodium, lithium, and mercury

(2) Generating long-time mechanical property data, particularly creep and stress rupture strength

(3) Designing, fabricating, and evaluating suitable hardware for prototype reactors.

North American Rockwell has measured the solubility of selected refractory-metal alloys in high-purity potassium and lithium (oxygen content of 6 and 33 ppm, respectively) over the range of 1200-1600 C (2190-2910 F).(1) Results, summarized in Table 1, confirmed data from earlier studies with the Cb-1Zr alloy, and show that additions of the reactive Group IVA metals (titanium, zirconium, and hafnium) dramatically reduce the apparent solubilities of tantalum and columbium in potassium and lithium. Except for rhenium (whose solubility was at the limit of analytical detection), all of the alloys at a given temperature were more soluble in potassium than lithium. This occurrence was ascribed to the greater contribution to the observed solubilities in potassium of the formation and the solution of complex alkali metal-refractory metal-oxygen compounds. This mechanism is less prevalent in lithium solutions containing low-oxygen concentrations because of the significantly greater tendency for oxygen (LiO_2) to remain dissolved in dilute solution in lithium.

TABLE 1. SOLUBILITY OF REFRACTORY METALS AND ALLOYS IN POTASSIUM AND LITHIUM(1)

Solute	Solubility, wppm in K	Temp Range, C	Solubility, wppm in Li	Temp Range, C
Ta from T-111(a)	$\log_{10}$ (wppm) = [illegible] - [illegible]/T°K	1,000-1600	[illegible]-5	1200-1600
Ta from ASTAR-811C(b)	6-10	1200-1600	[illegible]-3	1200-1600
Ta from Ta-0.5Zr	500-5000	1200-1600		
Nb from Cb-1Zr	<6	1200-1400		
Nb from Nb-0.5Zr	10-15	1200-1600		
Mo from Mo-0.5Zr	100	1200-1400		
Mo from TZM(c)	<12	1400		
Hf from ASTAR-811C(b)			6-30	1200-1600
Hf (zone refined)	<100		<6	1200-1400
Zr (zone refined)	60-190	900-1200		
W (vapor deposited)	10-80	1200-1600	[illegible]-3	1200-1600
Re	<1	1200-1600	[illegible]-2	1200-1600
Mo			2-15	1200-1600

(a) T-111: Ta-8W-2Hf
(b) ASTAR-811C: Ta-8W-1Hf-1Re-0.025C
(c) TZM: Mo-0.5Ti-0.07Zr

In a continuing Oak Ridge program, the creep-rupture properties of SU-16 alloy (Cb-11W-3Mo-2Hf-0.08C) bar stock were determined, for two conditions of heat treatment, as shown in Figure 1.(2) Similar tests on the SU-31 (Cb-17W-3.5Hf-0.12C) and C-129Y (Cb-10W-10Hf-0.1Y) alloys over the same temperature and time intervals are in process.

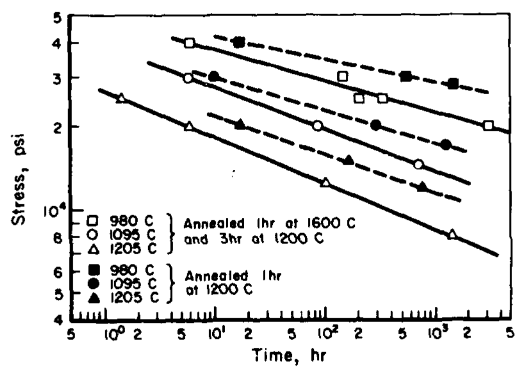

FIGURE 1. CREEP-RUPTURE PROPERTIES OF SU-16 ALLOY(2)

In related work at the Lawrence Radiation Laboratory, creep data were determined for tungsten and rhenium in a vacuum of 10^{-9} torr and are summarized in Figure 2.(3)

NASA-Lewis has completed the design and fabrication of a new, counterflow double-containment mercury boiler in their SNAP-8 program to develop a Rankine-cycle power system for space application.(4) This design features seven tantalum tubes for the containment of the mercury, with each of these tubes being placed inside a flattened stainless-steel tube. These tubes were coiled, bundled, and inserted in a coiled, larger diameter stainless-steel tube which

4

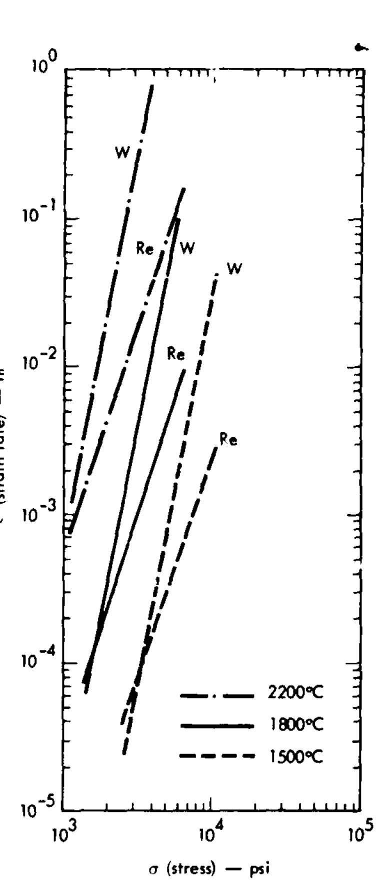

FIGURE 2. COMPARISON OF CREEP DATA FOR TUNGSTEN AND RHENIUM(3)

contains NaK from the primary loop (for carrying heat energy from the reactor). Tantalum was selected as the mercury containment material because of its excellent compatibility with mercury[5] (see Figure 3) as well as its good fabricability and weldability. The large differences in thermal expansion between the tantalum and the stainless-steel tubes was accomodated by the flattened stainless-steel tube, allowing the tantalum to radially move with respect to the stainless steel.

In operation, mercury enters the boiler at 500 F at a flow rate of 11,500 lb/hr and exits at 1275 F under 265 psia. The boiler has operated for 1444 hours including three full cycles from room temperature to 1300 F with no malfunctions. This same boiler, with minor external modifications, has since been operated at General Electric/Evendale in excess of 7000 hours.

In a more advanced NASA program, General Electric has the goal of completing a 10,000-hour refractory alloy evaluation in a Rankine System Corrosion Test Loop containing lithium and potassium in the primary and secondary loops, respectively.[6] The T-111 alloy (Ta-8W-2Hf) is serving as the containment alloy, and both Mo-TZC and the Cb-132M (Cb-20Ta-15W-5Mo-1.5Zr-0.12C) alloys are being evaluated as turbine candidate materials in the two-phase potassium circuit of the system. In the primary loop, lithium, heated to 2250 F by direct

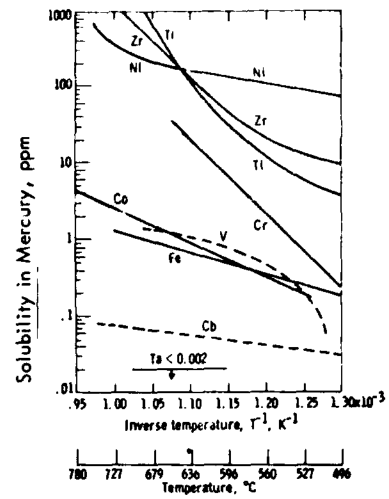

FIGURE 3. LIQUIDUS CURVES OF METALS IN HIGH-TEMPERATURE MERCURY(5)

resistance, is used to heat the potassium (via a heat exchanger) in the secondary loop to 2140 F. Temperatures of the potassium in the turbine simulators range from 2140 to 1435 F. As of April 19, 1969, this corrosion test loop had completed 2000 hours of stable operation under these conditions without any difficulty.

PHYSICAL-PROPERTY MEASUREMENTS

Investigators at the Bureau of Standards have determined the melting point, heat capacity, and electrical resistivity of molybdenum at temperatures above 2570 C (4660 F) using a dynamic pulse-heating technique.[7] The results of these determinations, summarized below, are generally in good agreement with earlier results of other workers:

Resistivity at 2607 C, 79.7 ohm-meters x 10^4

Heat Capacity at 2607 C, 52.4 joules/gm-atom

Melting Temperature, 2616 ± 8 C.

In an investigation implemented with mass spectroscopic and ultrahigh-vacuum techniques, solution and diffusion of hydrogen in tungsten were determined at pressures between 600 and 10^{-8} torr, and temperatures between 1100 and 2400 K (1520 and 3860 F).[8] The solubility constant, $S = 2.9 \times 10^{-1}\exp(-24000/RT)$ torr liter/cm^3 torr$^{1/2}$, and the diffusion constant, $D = 4.1 \times 10^{-3}\exp(-9000/RT)$ cm^2/sec were obtained, which in conjunction with literature values for the permeation constant, P, are consistent with the equation $P = SD$.

TENSILE PROPERTIES OF TUNGSTEN AND TUNGSTEN ALLOYS

At TRW, the stress-strain behavior of extruded tungsten bar has been investigated from room temperature to 5150 F, using a unique computerized electron-beam-heating procedure and a high-speed data system.[9] This arrangement permits heating rates of approximately 1000 F/second and a data recording rate of 640 lines per second to obtain stress-strain behavior for wrought tungsten under conditions not previously investigated. The greatest differences in data ob-

tained in this study as compared with published data for wrought tungsten were in those temperature ranges where rates of recrystallization or grain growth are most rapid. In these temperature ranges, the observed yield strength exceeded that obtained on wrought tungsten tested at a lower rate. Table 2 lists test time, strengths, and post-test grain size for a series of measurements.

The properties of tungsten-base-rhenium-hafnium-carbon alloys were evaluated by NASA to determine whether previously observed high-temperature strengthening effects of HfC in tungsten could be combined with the low-temperature ductilizing effect of dilute rhenium additions to tungsten.[10] The general conclusion from this study was that these two effects can be combined without detrimental interaction. The optimum alloy, W-4Re-0.35Hf-0.35C (atomic percent), was found to have a tensile strength of 60 to 70 ksi at 3500 F, Figure 4, and bend ductile-brittle transition temperatures of 200 and 540 F, Figure 5, in the as-rolled and solution-annealed conditions. The strength increment associated with HfC particles was found to be proportional to the square root of the mol percent of HfC and to decrease with increasing HfC particle size in accordance with recent dispersion-strengthening theory (Orowan mechanism). Growth of HfC particles was fairly rapid above 3500 F limiting this alloy to short-time use at these temperatures. Calculations indicated that, at lower temperatures, particle stability and high strengths should be maintained for hundreds to thousands of hours.

PREPARATION AND EVALUATION OF TUNGSTEN TUBING

Current developments in a program for the fabrication of tungsten tubing by extrusion of powder have been reported by Los Alamos.[11] Figure 6 illustrates the fabrication steps. Although a major problem in extruding refractory metal tubing has been the delayed cracking of the extruded tube in the green condition, it was prevented by drying at 230 F (110 C) immediately after extrusion to shape. Methocel and glycerin in water were found to be satisfactory in small amounts as binders for the extrusion of 0.7- to 1.3-micron tungsten powders. Tubing 95 to 96 percent dense having 0.410- to 0.210-inch OD and wall thicknesses of 0.100 to 0.025 inch were made.

At the Lawrence Radiation Laboratories, CVD W-25Re fine-grain tubing of 0.5-inch diameter with a 0.040-inch-thick wall has been made by optimizing reaction parameters.[3]

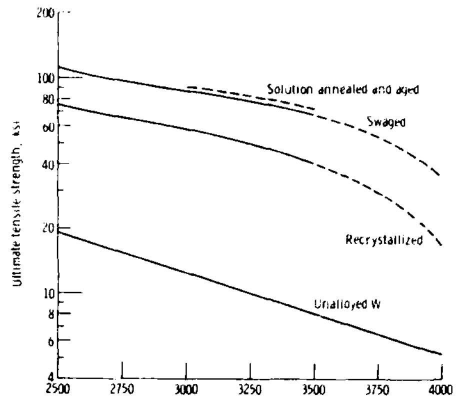

FIGURE 4. TENSILE STRENGTH OF OPTIMUM ALLOY COMPOSITION W-4Re-0.35Hf-0.35C COMPARED WITH STRENGTH OF UNALLOYED TUNGSTEN AT 2500 TO 4000 F[10]

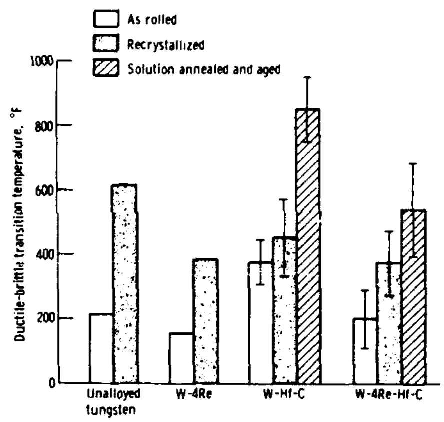

FIGURE 5. DUCTILE-BRITTLE TRANSITION TEMPERATURES FOR ARC-MELTED TUNGSTEN, W-4Re, W-Hf-C[10]

(Average values are shown for tungsten and W-4Re, while median values and average differences from median are shown for W-Hf-C and W-4Re-Hf-C.)

TABLE 2. TEST TEMPERATURES AND TIMES VERSUS MICROSTRUCTURAL CHANGE AND STRENGTH VALUES FOR A SERIES OF EXTRUDED TUNGSTEN TENSILE BAR SPECIMENS[9]

Test Temp., F	Elapsed Time From 2000 F to Start of Test, sec	Total Time Above 2000 F, sec	Grain Size, mm	0.2% Offset Yield Strength, ksi	Ultimate Tensile Strength, ksi
2060	2	20	Wrought	52	61
2140	4	22	Wrought	48	54
2700	7	23	Part. Recryst.	42	46
2730	13	70	Part. Recryst.	35	43
3120	16	89	0.0089	18	22
3260	13	107	0.0117	12	19
4160	30	153	0.0153	9	13
4250	24	147	0.0167	9	12
5150	24	160	0.022	6	8

Blend powders

Prepare binder solution

Mix powder and binder solution

Dry

Extrude

Low temperature thermal treatments (< 500 C)

1000 C sinter in H_2

1700 C sinter in H_2

2350 C sinter in vacuum

FIGURE 6. FLOW SHEET FOR PROCESSING OF POWDER-EXTRUDED TUNGSTEN TUBING

A test method was developed by NASA for determining the burst strength of 3/8-inch diameter and 1/2-inch diameter thin-walled tungsten tubing at high temperatures.(12) The tubes that were tested were made by (1) floating mandrel extrusions to size, (2) a proprietary method of extrusion and processing, (3) extrusion and drawing using the filled billet technique, (4) chemical vapor deposition from both WCl_6 and WF_6, and (5) electroforming from a fluroide bath. Measurements were made at temperatures ranging from 3000 to 4500 F using nitrogen gas as the internal pressurizing medium. The burst strengths of the majority of the tungsten tubes were equal to or greater than the ultimate tensile strength of extruded or swaged-extruded tungsten rod. Results for WCl_6-vapor-deposited tubes indicated that the process is capable of producing tubing which is as strong as wrought tungsten tubing.

REFERENCES

Eichelberger, R. L., McKisson, R. L., and Johnson, B. G., "Solubility of Refractory Metals and Alloys in Potassium and Lithium", Report NASA CR-1371, North American Rockwell Corporation, Canoga Park, Calif., Contract NAS 3-8507 (May, 1969).

(2) Preliminary information from Oak Ridge National Laboratory, Oak Ridge, Tenn.

(3) Roberts, Jr., L. W., and Root, G. S., "Refractory Alloy Development for the Advanced Space Power Reactor Program", Report UCRL-50603, University of California, Lawrence Radiation Laboratory, Livermore, Calif. (March 1969).

(4) Gertsma, L. W., and Medwid, D. W., "Design and Fabrication of a Counterflow Double-Containment Tantalum-Stainless Steel Mercury Boiler", Report NASA TN D-5092, NASA-Lewis Research Center, Cleveland, O. (May 1969).

(5) Weeks, J. R., "Liquidus Curves and Corrosion of Fe, Cr, Ni, Co, V, Cb, Ta, Ti, and Zr in 500-750 C Mercury", Corrosion, 23 (4), 98-106 (April 1967).

(6) Preliminary information from General Electric Company, Cincinnati, O., under NASA Contract NAS 3-6474.

(7) Cezairliyan, A., Morse, M. S., and Beckett, C. W., "Heat Capacity, Electrical Resistivity, and Melting Point of Molybdenum In the Melting Region", Chapter 1, Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds, NBS Report 10004 (AFSOR 69-1020TR), National Bureau of Standards, Washington, D. C. (January 1, 1969).

(8) Frauenfelder, R., "Solution and Diffusion of Hydrogen in Tungsten", Vacuum Science and Technology, 6 (3), 388-397 (May/June 1969).

(9) Janowski, K. R., and Bohn, J. R., "Stress-Strain Behavior of Rapidly Heated Wrought Tungsten", Report CONF-681031-1, TRW Systems Group, Redondo Beach, Calif.

(10) Klopp, W. D., and Witzke, W. R., "Mechanical Properties of Arc-Melted Tungsten-Rhenium-Hafnium-Carbon Alloys", Report NASA TN D-5348, NASA, Lewis Research Center, Cleveland, O. (July 1969).

(11) Erickson, W. C., and Javorsky, C. A., "Powder Extrusion of Tungsten Tubing", Report LA-4099, University of California, Los Alamos, N.M. (May 7, 1969).

(12) Gyorgak, C. A., "Burst Testing of Tungsten Tubing at Temperatures from 3000 to 4500 F (1650 to 2480 C)", Report NASA TM X-1843, NASA, Lewis Research Center, Cleveland, O. (July 1969).